Electric Conductors

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Supramolecular Conducting Nanowires from Organogels**

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The preparation of conducting nanoscopic fibers based on the self-assembly of π functional units is an interesting goal as they may be incorporated in molecular electronic devices.[1] This bottom-up approach[2] to supramolecular wires offers advantages over strictly covalent approaches, but controlling the self-assembly process is challenging. In particular, deposition on surfaces can be difficult to control, and different morphologies and size distributions are common. The gel state offers an interesting way to form fibers in a homogeneous medium (the matrix solvent),[3] which can then be physically deposited on any surface. Evaporation of the solvent leaves the xerogels as a mesh of interwoven fibers. For this reason, we are investigating gels based on functional molecules, and here we report the preparation of conducting nanowires based on a compound which can be readily prepared on a gram scale. We show that the as-prepared doped xerogel is a conductor in the bulk state, and shows a property unique for such a nanomaterial: when annealed, it undergoes a solid-state-like transition to a phase with conductivity an order of magnitude higher than that of the initial phase, and its local (nanometer-scale) transport properties can approach metallic conductivity.

The functional unit we have used is tetrathiafulvalene (TTF), because stacks of these units in their doped states conduct in single crystals.[4] TTFs can also form fibrous aggregates as a result of hydrophobic interactions in regions of their molecular structure,[5] through stacking interactions,[6] and during the formation of Langmuir layers.[7] Hydrogen bonds can be used to influence the disposition of TTF units in crystals;[8] for example, hydrogen bonds to amide groups have been shown to aid the formation of stacks of molecules.[9] Inspired by the latter example and amide-based gels,[10] we prepared amide-functionalized TTF **1** (Figure 1). It was considered a good candidate to form gels because it has: 1) an amide group which permits the formation of hydrogen bonds, as well as 2) a number of sulfur atoms in suitable positions such that short contacts can form between them in neighboring molecules, and 3) an alkyl chain which ensures van der Waals interactions between themselves and molecules of solvent.[11] It is also available in relatively large quantities from a two-step procedure which starts from precursors which are available on a multigram scale. Compound **1** (see the Supporting Information for characterization) shows the typical redox chemistry for this family of compounds, with a first oxidation to form a radical cation at approximately 0.56 V and a second one (to give the dication) at around 0.95 V. The first potential is easily accessible using chemical oxidants, and this offers a way to dope the samples.

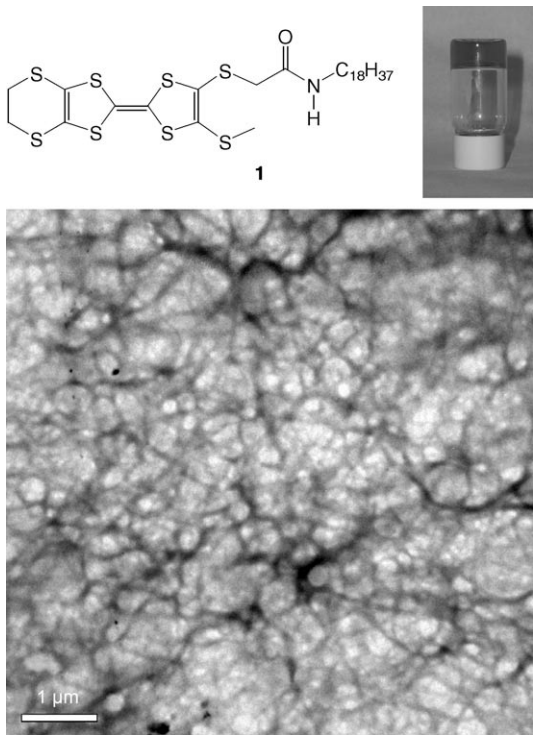

Figure 1. The chemical structure of **1**, a photograph of the organogel that it forms in hexane, and a TEM image of the unstained xerogel of **1** formed from hexane.

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Transparent orange organogels which are stable for several days are formed when **1** is dissolved in decane or hexane by heating to around 50 °C, then air cooled and left to stand. The compound is either soluble or precipitates from other solvents (see the Supporting Information). Derivatives of **1** with shorter alkyl chains (C_{12} or C_{15}) do not form gels. The IR spectra of the gels of **1** show the same characteristic band at approximately 3300 cm^{-1}, which is indicative of hydrogen-bonded N–H groups. The corresponding C=O stretching and N–H bending bands are observed at 1645 and 1551 cm^{-1}, respectively. Evaporation of the solvent from the hexane gel (which took place virtually immediately upon their deposition onto a KBr disc, as shown by recording the IR spectrum over several hours; see the Supporting Information) left a xerogel which gave essentially the same IR spectra as that of **1** in the gel and in the solid state, thus indicating that the hydrogen bonding is similar in the different materials. Therefore, the hydrogen bond to the amide group is sufficiently robust for the formation of hydrogen-bonded chains of this molecule. Transmission electron microscopy (TEM) images of the as-prepared xerogel formed on a holey carbon grid (by deposition of a sample of the gels) showed the presence of a complex network of fibers with lateral dimensions ranging from a few nanometers to several hundred nanometers, with the smaller fibers clearly crossing, intertwining, and fusing (Figure 1). To convert TTF-based fibers into conducting wires a mixed valence state must be generated, which, if the arrangement of the TTF units is appropriate, could result in charge transport within the fibers. The oxidation of donor molecules with iodine vapor is an easy way to generate this state.[12] If electrical contacts between the fibers (side-on contacts between the stacked TTFs) are good, it is possible to form a conducting network in the bulk state. We show that a simple synthetic procedure (see the Supporting Information) can be used to advantage in the preparation of conducting nanowires.

The xerogel of **1** was doped (oxidized) by exposure to iodine vapor. A very broad charge-transfer band between around 1000 and 7000 cm^{-1} was observed when a xerogel formed on the surface of a KBr disc was exposed to the oxidant (see the Supporting Information). The spectrum develops such that absorption maxima are formed at approximately 3000 cm^{-1} and 1245 cm^{-1}. These maxima are typical of a mixed-valence state of a material containing a TTF-derived species in the neutral and cation radical states.[13,14] The steady state is reached an hour after doping, which is in contrast to another gel system where the steady state is reached after a week.[15] The significant absorption between 6000 and 7000 cm^{-1} is presumably a consequence of aggregates of cation radicals which diffuse through the material with sufficient time to generate a uniform mixed-valence material. Importantly, the IR peaks associated with the amide groups (at 1645 and 1551 cm^{-1}) do not change after doping of the xerogel derived from **1**, nor do the peaks change position as a function of time after the oxidation process. This observation indicates that the hydrogen-bonded chain formed by the amide groups is not disrupted in the doping process. In accord with this hypothesis, the topography of the fibers after doping is indistinguishable from those of the as-formed xerogels (see the Supporting Information).

The electrical conductivity of the doped xerogel of **1** prepared on glass was studied using four-probe dc resistance measurements (see the Supporting Information). The room-temperature conductivity (σ) of the as-prepared doped xerogel was about $3–5\times10^{-3}\ \Omega^{-1}\,cm^{-1}$. The temperature dependence of the resistance in the range 200 to 310 K revealed a semiconductor-like behavior with an activation energy (E_{act}) of 170 ± 15 meV. This result provides basic evidence in support of the formation of conducting fibers which form a mesh that behaves as a semiconductor in this measurement. The value of E_{act} is very reproducible (tens of samples have been measured) and lies at the lower energy range seen for TTF-derived fibers produced in a liquid crystal and isolated by using a more complicated procedure.[15]

The as-prepared conducting xerogel samples were heat treated, as the transport properties of crystals of polyhalide TTF-based charge-transfer salts can be changed at high temperature through transformation of the structural phase.[16] The resistance decreases on warming the sample before reaching a minimum at around 325 K (Figure 2a);

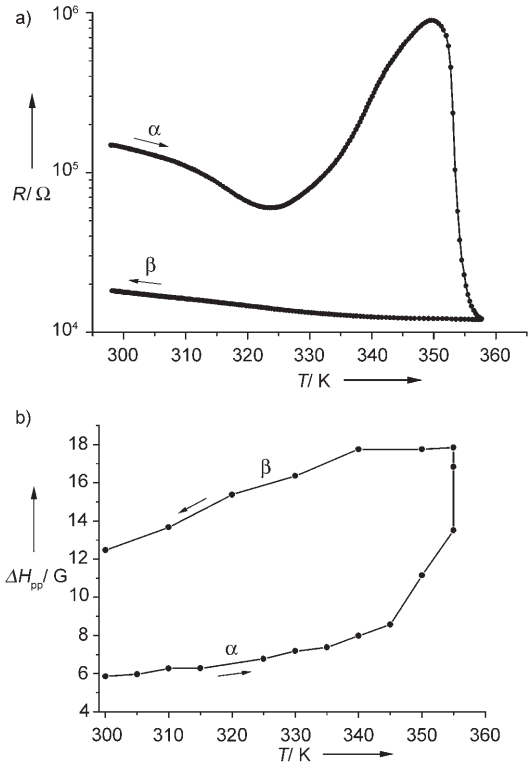

Figure 2. The temperature dependence of a) the resistance and b) the ESR linewidth of the as-prepared doped xerogel of **1**, showing the change of phase.

then it increases as the temperature increases, and above approximately 350 K drops by two orders of magnitude. Cooling the samples back to room temperature shows they have a new semiconductor-like behavior, with an activation energy of 80 ± 5 meV, which is much less than that of the as-prepared doped xerogel.

This kind of dramatic change in the $R(T)$ behavior at high temperatures indicates an irreversible phase transition from

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one phase (hereafter the α phase) of the doped xerogel to a thermally converted one (hereafter the β phase). The room-temperature resistivity of the β phase is less than that of the α phase by a factor of about 10. Another point worth noting in regard to the thermally converted β phase is that the high-temperature conversion is irreversible, thus suggesting that the β-phase xerogel is thermodynamically more stable than the as-prepared doped xerogel.

We used ESR spectroscopy to confirm the high-temperature phase transition, since the surrounding symmetry of each TTF-based radical cation in an organic conductor mainly determines the midpoint value of the peak-to-peak linewidth (ΔH_{pp}) of the single ESR signal.[17] The temperature dependence of the ESR spectrum of the sample in the range from 300 K to 355 K, with the static magnetic field oriented perpendicular to the surface of the sample, shows that the peak-to-peak linewidth smoothly increases from 6 G to 8 G (Figure 2b). Above 345 K, an irreversible change in the linewidth takes place: it jumps up from about 8.5 G to approximately 18 G. Also, there is a concurrent increase in the intensity of the ESR signal (see the Supporting Information). This data is proof of an irreversible structural-phase transition, as witnessed in the resistivity measurements. The origin of both the minimum and maximum resistance observed in the range $310 < T < 355$ K is not totally clear at present, but three processes are likely to contribute: 1) The diffusion of iodine away from the surface of the xerogel, 2) modification of the contacts between the nanofibers, and 3) the structural-phase transition, which is shown clearly in the ESR data.

Current-sensing (CS, or conductive) AFM is a useful probe for monitoring the pathways for electrical conduction in materials. In the experiment, topological and electrical signals are recorded as a metal-coated AFM tip is passed over the material. The texture seen from the CS AFM measurements on the thermally converted xerogel on graphite[18] shows areas with a fiberlike morphology (Figure 3a,b), and even areas with parallel nanofibers (Figure 3b). *I–V* responses collected during the CS AFM experiment show semiconducting character with a small gap (Figure 3c, curve 1, the curve flattens around zero potential). Moreover in some bright areas, where the current quickly saturates, some *I–V* responses with an apparently metallic character were observed (Figure 3c, curve 2). *I–V* responses collected from dark areas of AFM images have semiconductor character with a wide gap (Figure 3c, curve 3). Therefore, the local transport properties of the β phase observed over small distances have metallic character and result from the transport properties of supramolecular wires, which is in contrast to another system without strong hydrogen bonds between the donor molecules.[19] The *I–V* responses with semiconductor-like character are probably associated with a network of nanocontacts between these metallic wires. In support of this hypothesis, the intensity of the ESR signal stays remarkably constant in the range from 350 to 250 K (see the Supporting Information), indicative of Pauli-type behavior and metallic characteristics in these low-dimensional nanoscopic objects.

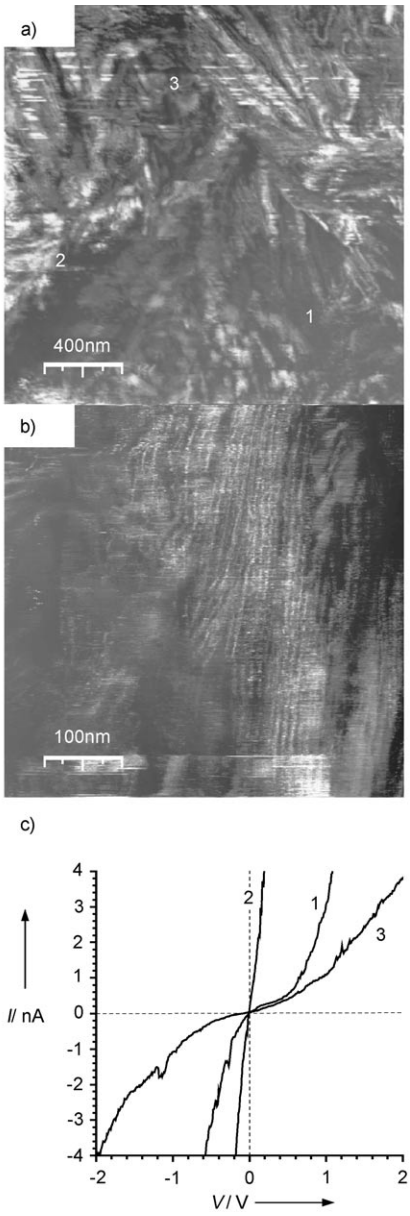

Figure 3. a, b) Current-sensing AFM images showing the current response of a doped annealed xerogel of **1** on graphite, and c) representative spectroscopic curves of different areas of the material which correspond to the numbered areas in image a.

In conclusion, the organogel formed by **1** is an excellent medium for the formation of nanofibers which can be transformed into conducting or even metallic nanowires by a simple doping and annealing procedure, which leads to a bulk material which conducts electricity. A structural phase change is observed in the as-prepared material, with the sample's resistance decreasing by an order of magnitude. This procedure allows the formation of stable TTF-based nanowires on different substrates and generation of a thin film which is electrically conducting. The hydrogen-bonding system acts as an excellent scaffold, and is the key to generating the conducting nanowires: The fibers are held robustly by them and they organize the functional units. The

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ease of the processing method makes it very appealing for applications in molecular electronics.

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